5

METHOD OF FORMING A CONDUCTIVE CONTACT

FIELD OF THE INVENTION

The present invention relates to the field of semiconductor device fabrication, and more particularly to methods for making conductive contacts in the formation of a semiconductor device.

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BACKGROUND OF THE INVENTION

As semiconductor fabrication moves toward maximizing circuit density, electrical components are formed at a number of layers and different locations. This requires electrical connection between metal layers or other conductive layers at different elevations in the substrate. Such interconnections are typically provided by forming a contact opening through insulating layer to the underlying conductive feature. With increasing circuit density, the dimensions of openings for electrical contacts become narrower and deeper, posing a challenge to provide adequate conductive fill within high aspect ratio openings.

Typically, in forming a contact plug, a thin layer of titanium is deposited over the top of a silicon base layer (substrate), and tungsten or other electrically conductive plug material is then deposited from tungsten hexafluoride (WF_6) by chemical vapor deposition (CVD) to fill the contact hole. However, there are several limitations of tungsten (W) plugs. Tungsten does not provide an adequate fill for high aspect ratio features. In addition, the use of WF_6 as a precursor gas in the formation of tungsten plugs, can result in the penetration of the fluoride component into the adjacent dielectric layer causing lateral encroachment and wormholes.

Titanium nitride (TiN) films have attractive properties that may overcome the limitations of tungsten plugs as integrated circuit (IC) devices continue to shrink below 0.15 micron dimension. TiN films have been deposited by low pressure chemical vapor deposition (LPCVD) using tetrakisdimethyl-amidotitanium (TDMAT) and ammonia as precursor gases. However, TDMAT films have a high carbon content and when subjected to high temperatures in the presence of oxygen, become porous and, therefore, are unusable as a conductive contact.

Thin TiN films and liners have also been deposited from titanium tetrachloride (TiCl$_4$) and ammonia (NH$_3$) by CVD onto a titanium (Ti) liner overlying the insulative layer. Although useful for forming a thin liner, when pure TiCl$_4$-based TiN is deposited to fill a via or other contact opening, the material does not adhere well to the Ti thin layer, particularly when the TiN layer becomes greater than about 150 to about 200 angstroms thick.

In addition, it has been found that chlorine (Cl$_2$) within a contact fill material such as TiN, which has been deposited from a chlorine-containing precursor such as TiCl$_4$, can diffuse into and corrode an overlying interconnect (e.g., aluminum), thus ruining the device.

Another problem lies in the formation of a conductive contact (e.g., contact plug) in a contact hole or via. Typically, a conductive material is blanket deposited over the surface of the substrate including into the contact hole, thus forming a continuous film. If an anneal is needed, the continuous film layer is typically subjected to a high temperature anneal, and then excess material is removed from the surface of the substrate by a chemical mechanical polishing (CMP) process, leaving the contact plug within the hole. A problem arises, however, during the high temperature anneal with cracking of the blanket material layer.

Therefore, it would be desirable to provide a conductive contact and a method of forming the contact that avoids such problems.

SUMMARY OF THE INVENTION

The present invention provides methods for forming conductive contacts in the construction of semiconductive devices, and the conductive components formed by those methods. The method is useful for fabricating contacts to electrical components beneath an insulation layer in an integrated circuit such as memory devices.

The present TiCl$_4$-based titanium nitride films are particularly useful as conductive contacts to replace tungsten (W) plugs in high aspect ratio features, particularly openings and other features having an aspect ratio of 3:1 or greater. The films also overcome inadequacies of pure TiCl$_4$-based titanium nitride films that are used as fill material for forming conductive contacts or interconnects within contact openings formed through an insulative layer of a semiconductor structure. Pure TiCl$_4$-based titanium nitride fills do not adhere well to the surface of insulative sidewalls of a contact opening, and can also

2

cause the insulative layer to crack due, at least in part, to the pressure exerted when the thickness of the

fill within the contact opening is about 200 angstroms or greater.

The present invention overcomes the problems of a pure TiCl$_4$-based titanium nitride plugs or

barrier film by incorporating diborane (B$_2$H$_6$) into the gas mixture to dope the TiCl$_4$-based titanium

5   nitride film during the deposition process. The addition of B$_2$H$_6$ to the precursor gas used to form the

TiCl$_4$-based titanium nitride film has been found to improve the mechanical properties of the resulting

titanium nitride film with substantially no impact on its conductive properties. In particular, the gaseous

mixture used to form the boron-doped, titanium nitride contacts comprises diborane (B$_2$H$_6$) in an amount

effective to provide a contact having an amount of boron to provide a level of adhesion of the

10   conductive contact to the insulative sidewalls of the contact opening to substantially eliminate peeling of

the contact from the sidewalls and cracking of the body of the insulative layer. The mixture further

includes an amount of ammonia (NH$_3$) to provide the contact with a level of nitrogen effective to

maintain the conductivity of the contact at a predetermined level for an effective electrical contact with a

conductive or active area within the substrate to/from an active area within a semiconductor device

15   and/or a memory or logic array.

However, one drawback of titanium nitride films formed from TiCl$_4$, including the boron-doped

films described herein, is that the chlorine (Cl$_2$) within the formed contact can diffuse into an overlying

material, for example, an overlying interconnect of aluminum, and corrode and ruin the device. It has

been found that a high temperature anneal of the TiCl$_4$-based titanium nitride film in a nitrogen-

20   containing atmosphere, preferably ammonia (NH$_3$), removes excess Cl$_2$ from the contact material to

overcome the diffusion problem. It has also been found that conducting a CMP process to remove

excess material from the substrate prior to the anneal step avoids undesirable problems with cracking of

the film layer and the wafer substrate.

In one aspect, the invention provides methods for forming a contact in a via or other contact

25   opening of a semiconductor structure. The opening is formed through an insulative layer to a

conductive or active area, such as a source/drain region, in an underlying silicon substrate. The method

is particularly useful for forming contacts within vias and other openings having an aspect ratio of about

3:1 or greater, and a width dimension of about 0.25 μm or less.

According to an embodiment of the method of the invention, a conductive material is blanket

30   deposited over the substrate to fill the opening, and excess material is removed from the surface,

3

preferably by chemical-mechanical polishing (CMP), with the conductive material remaining in the opening to form the contact. The contact is then heated to a high temperature, preferably by use of a rapid thermal anneal process, in a reactive gas to remove an undesirable component from the contact material.

5   In an example of this embodiment of the method, a titanium nitride contact can be formed by first depositing a seed layer comprising titanium silicide ($TiSi_x$) over the silicon substrate at the bottom of the contact opening, preferably to a thickness of about 250 to about 300 angstroms, for example, from a plasma source gas comprising titanium tetrachloride ($TiCl_4$) and hydrogen (H_2) by plasma-enhanced chemical vapor deposition (PECVD). A titanium nitride or boron-doped titanium nitride film (i.e.,

10   titanium boronitride, TiB_xN_y) can then be deposited onto the seed layer to fill the contact opening, typically to a thickness of about 1000 to about 3000 angstroms. The film layer can be deposited from a source gas mixture of $TiCl_4$, NH_3, and one or more carrier gases, with the addition of B_2H_6 to form the boron-doped layer, by thermal CVD at a pressure of about 1 to about 15 Torr and a temperature of about 550 to about 700°C. The substrate is then processed, preferably by CMP, to remove excess material

15   from the substrate while leaving the titanium nitride material in the contact opening. The contact is then subjected to a high temperature in a nitrogen-containing gas, preferably ammonia (NH_3) at above 700°C. with a rapid thermal anneal, to remove a high percentage of the chlorine (Cl_2) content from the contact material, preferably up to about 99% by wt.

     In another example of the method of the invention, a multi-layered titanium nitride contact is

20   formed within a contact opening of a semiconductive structure. A titanium silicide seed layer is first formed over the silicon substrate at the bottom of the contact opening. To form the layered contact, alternating layers of titanium nitride and boron-doped titanium nitride can then be deposited over the seed layer. In forming the alternating layers, a layer comprising titanium nitride (undoped) can be deposited from a first gaseous mixture comprising $TiCl_4$ and NH_3, to form a layer typically about 100 to

25   about 500 angstroms thick. Diborane (B_2H_6) can then be introduced into the gaseous mixture to deposit an intermediate layer of boron-doped titanium nitride to form a layer typically about 100 to about 500 angstroms thick. The flow of diborane into the gas mixture can then be stopped to deposit a next layer of titanium nitride layer that is not doped to a typical thickness of about 100 to about 500 angstroms. Additional alternating layers of doped and undoped titanium nitride can be deposited to

30   fill the opening, with the uppermost layer being undoped titanium nitride. Excess material is then

4

removed from the substrate by CMP, and the contact is subjected to a heat treatment, preferably by a rapid thermal anneal, preferably in ammonia at greater than 700°C., to decrease the chlorine (Cl_2) content of the contact.

Another aspect of the invention is a conductive contact formed in a semiconductor structure of a semiconductor circuit. The semiconductor structure comprises a silicon substrate, an overlying insulative layer, a contact opening formed through the insulative layer to expose the underlying silicon substrate, and the conductive contact formed within the opening.

In one embodiment of a contact according to the invention, the contact comprises a thermally annealed layer of titanium nitride and/or boron-doped titanium nitride overlying a titanium silicide layer formed over the substrate at the bottom of the opening, the contact having a low chlorine (Cl_2) content, preferably less than about 1% by wt.

In another embodiment, the conductive contact comprises multiple layers of thermally annealed titanium nitride overlying a titanium silicide layer deposited onto the silicon substrate at the bottom of the contact opening, the contact having a low chlorine (Cl_2) content, preferably less than about 1% by wt. The contact comprises alternating, overlying layers of undoped and boron-doped titanium nitride that fill the contact opening. An undoped titanium nitride layer overlies the titanium silicide layer, and also forms the uppermost layer of the conductive contact. The thickness of each of the individual layers is typically about 100 to about 500 angstroms.

Another aspect of the invention is an integrated circuit (IC) device that includes the foregoing conductive contacts comprising titanium nitride and/or boron-doped titanium nitride. The IC device comprises an array of memory or logic cells, internal circuitry, and at least one generally vertical conductive contact coupled to the cell array and internal circuitry.

In one embodiment of an integrated circuit device according to the invention, the IC device comprises a conductive contact comprising a thermally annealed titanium nitride and/or boron-doped titanium nitride fill that is formed within an insulative contact opening over a thin layer of titanium silicide deposited onto the exposed substrate at the bottom of a contact opening, and has a low chlorine (Cl_2) content, preferably less than about 1% by wt. In another embodiment of an integrated circuit device, the conductive contact comprises thermally annealed material having a reduced chlorine (Cl_2) content, preferably less than about 1% by wt., that is multi-layered, comprising alternating layers of titanium nitride (undoped) and boron-doped titanium nitride deposited onto a titanium silicide layer

overlying the substrate at the bottom of a contact opening. The contact is in electrical contact with an active area such as a source/drain region of a transistor or a memory or logic cell array, or other semiconductor device.

Advantageously, the present film overcomes limitations of tungsten plug fills in high aspect ratio devices, with parametric data showing superior results compared to that of tungsten. The films also have a decreased level of undesirably components such as chlorine that become incorporated into the film upon deposition of precursor gases to form the film. The present method provides a process of removing undesirable components such as chlorine and the like, from a contact which overcomes problems in the art with cracking from anneal processing steps, and without adversely effecting other structures and devices formed on the substrate. The present invention provides processes for forming conductive contacts that are fast, simple and inexpensive to implement in semiconductor manufacturing.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings, which are for illustrative purposes only. Throughout the following views, the reference numerals will be used in the drawings, and the same reference numerals will be used throughout the several views and in the description to indicate the same or like parts.

FIG. 1A is a diagrammatic cross-sectional view of a semiconductor wafer fragment at a preliminary step of a processing sequence.

FIGS. 1B through 1D are views of the wafer fragment of FIG. 1A at subsequent and sequential processing steps, showing fabrication of a conductive contact according to an embodiment of the method of the invention.

FIGS. 2A through 2F are views of the wafer fragment of FIG. 1A at subsequent and sequential processing steps, showing fabrication of a conductive contact according to another embodiment of the method of the invention.

FIGS. 3A and 3B are graphical depictions showing the amount of thermal stress (Gdynes/cm^2) versus diborane (B$_2$H$_6$) flow over a range of 200 to 600 sccm at reactor temperatures of 600°C. and 650°C.

6

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention encompasses methods of making integrated circuits, particularly methods for forming conductive contacts for providing electrical connection between conductive or active areas of discrete semiconductor devices or portions of such devices. In particular, the invention relates to

5 methods of forming a conductive contact having a reduced concentration of unwanted constituents such as chlorine that become incorporated into the contact, for example, from precursors, during formation. The invention further relates to a contact structure incorporating a titanium nitride and/or a boron-doped titanium nitride film having a low chlorine content. The present invention is particularly useful in providing a conductive contact in openings and other features having a high aspect ratio of 3:1 or

10 greater.

The invention will be described generally with reference to the drawings for the purpose of illustrating the present preferred embodiments only and not for purposes of limiting the same. The figures illustrate processing steps for use in the fabrication of semiconductor devices in accordance with the present invention. It should be readily apparent that the processing steps are only a portion of the

15 entire fabrication process.

Integrated circuits include a large number of electronic semiconductor devices that are formed on varying levels of a semiconductor substrate. Exemplary semiconductor devices include capacitors, resistors, transistors, diodes, and the like. In manufacturing an integrated circuit, the discrete semiconductor devices that are located on nonadjacent structural levels are electrically connected, for

20 example with an interconnect or conductive contact structure. The conductive contact generally comprises a region of conducting material that is formed between the semiconductor devices or portions of the semiconductor devices that are being placed in electrical communication. The conductive contact serves as a conduit for delivering electrical current between the semiconductor devices. Specific types of conductive contact structures include local interconnects, contacts, buried contacts, vias, plugs, and

25 filled trenches. The present invention particularly deals with the method of making conductive contacts that are used in the fabrication of semiconductor devices.

In the current application, the terms "semiconductive wafer fragment" or "wafer fragment" or "wafer" will be understood to mean any construction comprising semiconductor material, including but not limited to bulk semiconductive materials such as a semiconductor wafer (either alone or in

30 assemblies comprising other materials thereon), and semiconductive material layers (either alone or in

assemblies comprising other materials). The term "substrate" refers to any supporting structure including, but not limited to, the semiconductive wafer fragments or wafers described above. The term "undesirable component" refers to any element or compound contained within the contact material that will adversely affect a semiconductor device, for example, a high concentration of chlorine that can

5   corrode an overlying aluminum interconnect and adversely affect the device.

A first embodiment of a method of the present invention is described with reference to **FIGS. 1A-1D**, in a method of forming a conductive contact 34.. In the illustrated example, the contact 34 comprises titanium nitride or boron-doped titanium nitride. The contact is illustrated and will be described as being coupled to a diffusion region. However, the contacts of the present invention can be

10   used wherever required within the structure of a semiconductor circuit.

Referring to **FIG. 1A**, a semiconductive wafer fragment 10 is shown at a preliminary processing step. The wafer fragment 10 in progress can comprise a semiconductor wafer substrate or the wafer along with various process layers formed thereon, including one or more semiconductor layers or other formations, and active or operable portions of semiconductor devices.

15   The wafer fragment 10 is shown as including a silicon-comprising base layer or substrate 12. An exemplary substrate 12 is monocrystalline silicon that is typically lightly doped with a conductivity enhancing material. Formed at the surface 14 of the substrate 12 are a transistor structure 16 and an overlying insulative layer 18. The transistor 16, comprising a gate 20 and adjacent source/drain diffusion regions 22a, 22b, can be formed by conventional methods known and used in the art.

20   The insulative layer 18 comprises an oxide, for example, silicon dioxide (SiO_2), phosphosilicate glass (PSG), borosilicate glass (BSG), and borophosphosilicate glass (BPSG), in a single layer or multiple layers, being BPSG in the illustrated embodiment. The BPSG insulative layer 18 has been etched using a known photolithography technique, for example, reactive ion etching (RIE), while masking with a patterned photoresist layer (not shown) to provide a via or other contact opening 24

25   defined by insulative sidewalls 26 and a bottom portion 28. The contact opening extends to the diffusion region 22a (i.e., source/drain region) in the underlying silicon substrate 12 to which electrical contact is to be made.

Referring to **FIG. 1B**, a titanium silicide ($TiSi_x$) seed layer 30 is formed over the exposed surfaces 14, 18 respectively, of the silicon substrate at the bottom 28 of the contact opening 24 and the

30   insulative layer 18. Typically, the seed layer is formed to a thickness of about 250 to about

8

300 angstroms. The resulting TiSi$_x$ seed layer 30 that forms at the interface with the diffusion region 22a is useful to lower resistance in the contact region. Techniques and process systems for forming a titanium silicide layer are well known in the art, as described, for example, in U.S. Patent No. 6,086,442 (Sandhu, et al.) and No. 5,976,976 (Doah, et al.), the disclosures of which are incorporated by reference

5   herein.

Preferably, the TiSi$_x$ seed layer 30 is formed by a conventional plasma enhanced chemical vapor deposition (PECVD) process that comprises forming an RF plasma from source gases comprising titanium tetrachloride (TiCl$_4$), hydrogen (H$_2$), a silicon precursor such as silane (SiH$_4$) or dichlorosilane (SiH$_2$Cl$_2$), and carrier gases such as argon (Ar) and/or helium (He) to deposit a layer of titanium silicide

10   (TiSi$_x$) over the substrate (silicon) surface 14 and the surface 19 of the insulative layer 18. Exemplary process conditions for achieving the formation of the TiSi$_x$ seed layer 30 include a temperature of about 650°C., a process pressure of about 0.5 to about 20 Torr, an rf power range of about 400 watts, and flow rates of about 150 to about 300 sccm TiCl$_4$, about 1000 to about 8000 sccm hydrogen (H$_2$), about 1 to about 100 sccm silane (SiH$_4$), about 1000 sccm argon (Ar), and about 50 sccm nitrogen (N$_2$).

15   Although the preferred process for forming the TiSi$_x$ seed layer is by PECVD technique, the TiSi$_x$ seed layer 30 can also be formed by a depositing a thin layer of titanium by physical vapor deposition (PVD), i.e., sputtering, onto the surface 14 of the substrate 12 at the bottom of the contact opening, and then performing an anneal step (about 650°C.) in an ambient gas such as nitrogen, argon, ammonia, or hydrogen. This causes the titanium to react with the silicon exposed on the surface 14 of

20   the diffusion region 22a to form the TiSi$_x$ seed layer 30. Such a process is said to be self-aligning, as the TiSi$_x$ is only formed where the titanium metal contacts the silicon active regions.

Another example of a method to deposit the TiSi$_x$ seed layer 30 is by a conventional low pressure CVD (LPCVD) process. Exemplary process conditions include a process temperature of about 650°C. to about 900°C., and a pressure of about 10 mTorr to about 1 Torr, using titanium tetrachloride

25   (TiCl$_4$) plus a silicon precursor or source gas such as silane (SiH$_4$) or dichlorosilane (SiH$_2$Cl$_2$) at a ratio of about 5:1, in a carrier gas such as helium.

To overcome the problems that occur in the use of a pure TiCl$_4$-based titanium nitride plug or contact, such as peeling of the contact from the insulative sidewalls of the contact opening and cracking of the insulative layer, the invention utilizes a boron-doped, TiCl$_4$-based titanium nitride fill (titanium

30   boronitride) to form the conductive contact or plug. Preferably, the foregoing conductive contact is

9

formed by a conventional thermal chemical vapor deposition (TCVD) process. Such TCVD techniques and process systems are well known in the art, as described, for example, in U.S. Patent No. 6,037,252 (Hillman et al.), and No. 5,908,947 (Iyer and Sharan), the disclosures of which are incorporated by reference herein. TCVD systems include standard thermal reactors such as cold wall/hot substrate

5   reactors and hot wall reactors, plasma-assisted reactors, radiation beam assisted reactors, and the like.

Typically, in a TCVD process, the substrate is placed in a reaction chamber (not shown) in which the substrate and/or the gaseous precursor is heated. Preferably, the substrate is heated to a temperature in excess of the decomposition temperature of the precursor gases. When the gases are introduced into the reaction chamber and brought into contact with the substrate, the gases decompose on the surface of

10   the substrate to deposit the titanium boronitride film comprising the metal and elements of the precursor or reactant gases.

In an exemplary TCVD process to deposit a titanium nitride (TiN) or boron-doped TiN (TiBxNy) layer according to the invention using hot or cold wall thermal chemical vapor deposition, the wafer fragment 10 is positioned in the TCVD reactor (not shown) and a source gas comprising titanium

15   tetrachloride ($TiCl_4$), ammonia (NH_3), one or more inert carrier gases such as argon, helium and/or nitrogen, and diborane (B_2H_6) to form a boron-doped TiN layer, is flowed into the reactor under conditions effective to chemical vapor deposit a layer 32 of $TiCl_4$-based titanium (doped or undoped) nitride over the titanium silicide ($TiSi_x$) seed layer 30 within the contact opening 24. The gaseous material is blanket deposited to a thickness to completely fill the contact opening, resulting in the

20   structure shown in **FIG. 1C**. Preferred flow rates of the precursors are about 100 to about 500 sccm $TiCl_4$, about 100 to about 1000 sccm NH_3, and about 100 to about 1000 sccm B_2H_6 (for a boron-doped film). The preferred temperature within the reactor (hot wall) or of the susceptor (cold wall) is from about temperature of about 550 to about 700°C., preferably about 560 to about 650°C., with pressure conditions within the reactor being from about 1 Torr to about 15 Torr, preferably about 10 Torr.

25   Typically, to fill a contact opening, about 1000 to about 3000 angstroms of material is typically deposited.

High-aspect-ratio contacts (aspect ratio of 3:1 or greater) that are made of $TiCl_4$-based TiN without the inclusion of B_2H_6 in the source gas, and have a thickness greater than about 150 to about 200 angstroms, possess a reduced level of adherence to the insulative sidewalls of a contact opening.

30   This results in the contact peeling away from the sidewalls of the opening. In addition, when such

10

contacts reach a thickness of about 200 angstroms or more, the high thermal stress of the fill material can cause cracking of the insulative layer. With the addition of increasing amounts of B_2H_6 to the $TiCl_4$ and NH_3 gaseous components, there is an increase in the adhesion of the fill material of the contact 34 with the insulative sidewalls 26 of the opening 24, and a reduction in the thermal stress level, which

5 substantially eliminates cracking of the insulative layer 18. However, as the amount of boron increases, there is also a reduction in the level of conductivity (and increase in resistance) of the contact 34. To counteract this effect, the ammonia in the gas mixture is provided in an amount effective to maintain the conductivity of the formed contact 34 at a predetermined level for an effective electrical contact with the diffusion area 22a or other semiconductor structure.

10 The inclusion of B_2H_6 in the source gas results in a $TiCl_4$-based, boron doped titanium nitride conductive layer 32 having the general formula TiB_xN_y (titanium boronitride). Such films are particularly useful as a fill in high-aspect-ratio contact openings and vias, particularly those having an aspect ratio of 3:1 or greater. The amounts of the B_2H_6 and the NH_3 gases that are flowed into the system are maintained so as to provide a fill having a level of adherence to the insulative sidewalls 26 of

15 the contact opening 24 such that the formed contact 34 remains attached to and does not peel away from the sidewalls, and no substantial cracks develop in the body of the insulative layer 18.

After deposition of the titanium nitride (doped or undoped) fill material, excess material 32 is removed from the surface 19 of the insulative layer, leaving the fill in the opening 24 to form the conductive contact or plug 34, as shown in **FIG. 1D**. The contact 34 provides electrical connection

20 to/from the diffusion region (conductive area) 22a to various parts of the semiconductor device. The excess material 32 can then be removed according to a conventional method known in the art, preferably, by chemical mechanical polishing (CMP).

The contact 34 is then subjected to a heat treatment, preferably with a rapid thermal anneal process, to at least about 700° C., preferably about 700 to about 800° C., in a nitrogen-containing gas,

25 preferably ammonia (NH_3), for a time of up to about 20 seconds, to drive out chlorine (Cl_2) incorporated into the contact from the $TiCL_4$ precursor during deposition. Preferably, the heat treatment reduces the concentration of chlorine in the contact by at least about 50% by wt., preferably by at least about 75% by wt., more preferably by at least about 95% by wt.

Advantageously, the present process of first removing the excess contact material by CMP, and

30 then thermally annealing the titanium nitride fill material remaining as the contact 34 in a

11

nitrogen-containing gas such as ammonia, reduces the chlorine content in the fill material without significantly changing the other properties of the film stack, particularly the advantages provided by the incorporation of boron into the film layer.

The resulting contact 34 comprises a titanium nitride layer (boron-doped or undoped) overlying a titanium silicide layer deposited onto the substrate at the bottom of the contact opening. The contact 34 possesses a reduced level of chlorine (Cl_2) as a result of the thermal anneal in ammonia (NH_3) or other nitrogen-containing gas. Preferably, the chlorine content of the contact following the anneal is less than about 4% by wt., preferably less than 3% by wt., more preferably less than about 1% by wt. Boron-doped titanium nitride contacts also possess a high level of adhesion to the insulative sidewalls of the opening, have a sufficiently low thermal stress level, measured in force per unit area (i.e., Gdynes/cm^2), to substantially eliminate cracking of the insulative layer, and are highly conductive with low electrical resistivity.

Although not shown, a passivation layer can then be formed over the device. Optionally, other interconnects and contact structures (not shown) can be formed overlying the present structure.

In another embodiment of the method of the invention, a multi-layered boron-doped and undoped titanium nitride contact can be fabricated in a wafer fragment, as depicted in **FIGS. 2A-2F**.

Referring to **FIG. 2A**, a wafer fragment 10' is shown before processing. Briefly, wafer fragment 10' includes a silicon-comprising substrate 12', for example, monocrystalline silicon, with an active area 22a' such as a source/drain region. An overlying insulative layer 18' comprising, for example, BPSG, has an exposed surface 19' and a contact opening 24' having sidewalls 26' and a bottom portion 28'. The contact opening 24' extends to the active area 22a'.

Referring to **FIG. 2B**, a thin titanium silicide ($TiSi_x$) layer 30' is formed over the active area 22a' at the bottom 28' of the opening 24'. The $TiSi_x$ layer 30' preferably has a thickness of about 250 to about 300 angstroms. The $TiSi_x$ layer 30' can be formed by conventional methods, as previously described, and preferably by PECVD using $TiCl_4$, H_2, and one or more carrier gases.

A layered contact is formed by depositing alternating layers of $TiCl_4$-based titanium nitride and a boron-doped $TiCl_4$-based titanium nitride into the contact opening, such that a boron-doped titanium nitride layer is interposed between two layers of non-doped titanium nitride. The multi-layered contact can be formed by conventional thermal CVD processing at a temperature of about 550 to about 700°C.,

12

preferably about 560 to about 650°C., and a pressure of about 1 Torr to about 15 Torr, preferably about 10 Torr.

A gas mixture comprising titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) and one or more carrier gases can be flowed into the reactor to form a layer 36a' of non-doped titanium nitride onto the $TiSi_x$ seed layer 30' to a desired thickness, typically about 100 to about 500 angstroms, resulting in the structure shown in **FIG. 2C**. Preferred flow rates for the gas mixture are about 100 to about 500 sccm $TiCl_4$ and about 100 to about 1000 sccm NH_3.

As shown in **FIG. 2D**, diborane (B_2H_6) is then flowed into the reactor, and a layer 32' comprising boron-doped, titanium nitride is deposited onto the non-doped titanium nitride layer from a gas mixture comprising $TiCl_4$, NH_3, and B_2H_6. The boron-doped, titanium nitride layer 32' is deposited to a desired thickness of about 100 to about 500 angstroms. Preferred flow rates for the gas mixture are about 100 to about 500 sccm $TiCl_4$, about 100 to about 1000 sccm NH_3, and about 100 to about 1000 sccm B_2H_6. As previously discussed, the flow of NH_3 and B_2H_6 can be controlled to modify the adhesiveness, thermal stress level, and conductivity of the resulting multi-layered contact.

The flow of B_2H_6 is then ceased, and the first source gas mixture (i.e., $TiCl_4$, NH_3) is flowed into the reactor to form a layer 36b' comprising undoped titanium nitride, as shown in **FIG. 2E**. The titanium nitride layer 36b' is deposited to a desired thickness, typically about 100 to about 500 angstroms. The titanium nitride layer 36b' can be deposited to fill the opening. Alternatively, additional layers of boron-doped titanium nitride can be deposited between two layers of non-doped titanium nitride as desired to fill the contact opening 24', with the uppermost layer of the contact comprising non-doped titanium nitride.

Excess fill material is then removed as depicted in **FIG. 2F**, for example, by CMP, to form the conductive contact 34'.

The contact 34' is then subjected to a thermal anneal at an elevated temperature, preferably greater than 700°C, preferably about 700°C. to about 800°C., in a nitrogen-containing atmosphere, preferably ammonia (NH_3), to drive the chlorine (Cl_2) deposited from the $TiCl_4$ precursor out of the contact material.

Sandwiching a layer of boron-doped titanium nitride 32' between undoped titanium nitride substantially reduces the thermal stress in a $TiCl_4$-based TiN fill material. This allows the fill to be used as a conductive contact to replace tungsten (W) plugs in high aspect ratio features. The combination of

13

alternating layers achieves a TiCl$_4$-based TiN contact having a level of adhesion that substantially eliminates peeling of the formed contact from the sidewalls of the contact opening. It also provides a lowered level of thermal stress that substantially reduces cracking of the body of the insulative layer, particularly when the thickness of the contact reaches about 500 angstroms or greater. In addition, the

5   resulting contact has a high level of conductivity for an effective electrical contact to a diffusion region or other conductive structure. The removal or reduction of chlorine (or other component) from the contact material by a high temperature anneal in ammonia (or other reactive gas) provides a contact having increased compatibility with an adjacent or overlying conductive material, for example, an aluminum interconnect. In addition, conducting the thermal anneal step after removing excess

10   conductive material from the surface of the substrate eliminates problems encountered with cracking of the film layer and/or the substrate with thermal anneals performed on a blanket material layer overlying the substrate.

EXAMPLE 1

15   A boron-doped TiCl$_4$-based titanium nitride (TiN) contact was formed in a high aspect ratio opening of a BPSG layer, without removal of chlorine by RTP anneal. The flow of diborane (B$_2$H$_6$) was varied over a range to test the change in thermal stress (Gdynes/cm^2) of the boron-doped, TiCl$_4$-based TiN contact on the BPSG insulative layer.

A wafer fragment was provided that had a silicon substrate layer and an overlying layer of

20   BPSG. A contact opening was formed through the BPSG layer. The aspect ratio of the opening was 10:1.

The TiCl$_4$-based TiN film was deposited by thermal CVD at a pressure of 10 Torr using a Centura system, available from Applied Materials company of Santa Clara, California. The precursor gases were flowed into the reactor as follows: 340 sccm TiCl$_4$, 200 sccm NH$_3$, 3000 sccm argon (Ar),

25   and 2000 sccm gaseous nitrogen (N$_2$). The diborane (B$_2$H$_6$) was flowed into the reactor at a rate ranging from 200 sccm to 600 sccm. Data was measured at two different temperatures: 600°C. and 650°C.

The results are shown in a graphical form in **FIGS. 3A and 3B**. As indicated, as the amount of boron (i.e., B$_2$H$_6$) was increased, the stress (Gdynes/cm^2) of the TiCl$_4$-based TiN material decreased to a neutral or zero stress level and below. Thus, by varying the B$_2$H$_6$ flow, the thermal stress of the

14

TiCl$_4$-based TiN film can be adjusted such that the material does not cause the insulative layer (e.g., BPSG) to crack.

EXAMPLE 2

A boron-doped TiCl$_4$-based titanium nitride (TiN) contact was formed in a high aspect ratio opening of a BPSG layer according to the method of the invention. A boron-doped TiN film was formed in a contact opening (10:1 aspect ratio) in a BPSG layer overlying a silicon substrate, as described in Example 1.

Excess titanium nitride film material was removed from the surface of the BPSG layer by conventional CMP, leaving the film material within the contact opening. The wafer was then subjected to a high temperature anneal by rapid thermal processing (RTP) in an ammonia (NH$_3$) atmosphere at 750°C for 25 seconds. PEELS micrographs showed differences in the chlorine (Cl$_2$) content of the boron-doped titanium nitride material before and after the high temperature anneal.

In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.